

# THF Dehydration by Pervaporation with Perfluorinated Composite Membrane

**Dan Campos**  
**Jeff Knopf**  
**Sudip Majumdar**  
**Stuart Nemser**

Compact Membrane Systems, Inc., Delaware, USA

[www.compactmembrane.com](http://www.compactmembrane.com)

8 June 2011

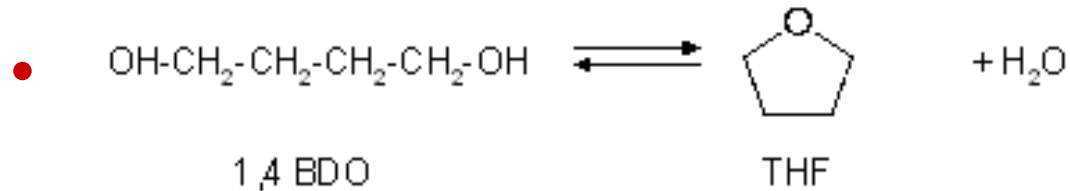
**NAMS 2011**  
June 4-8, 2011, Las Vegas, NV USA



# Presentation Outline

- THF background
- CMS membrane background
- H<sub>2</sub>O/THF pervaporation data
- Fouling resistance
- THF resistant module components
- Azeotropic distillation
- Concluding Remarks

# THF Background



- 99.95% minimum required purity
- Azeotrope @94.7% THF
- B.P. 66°C

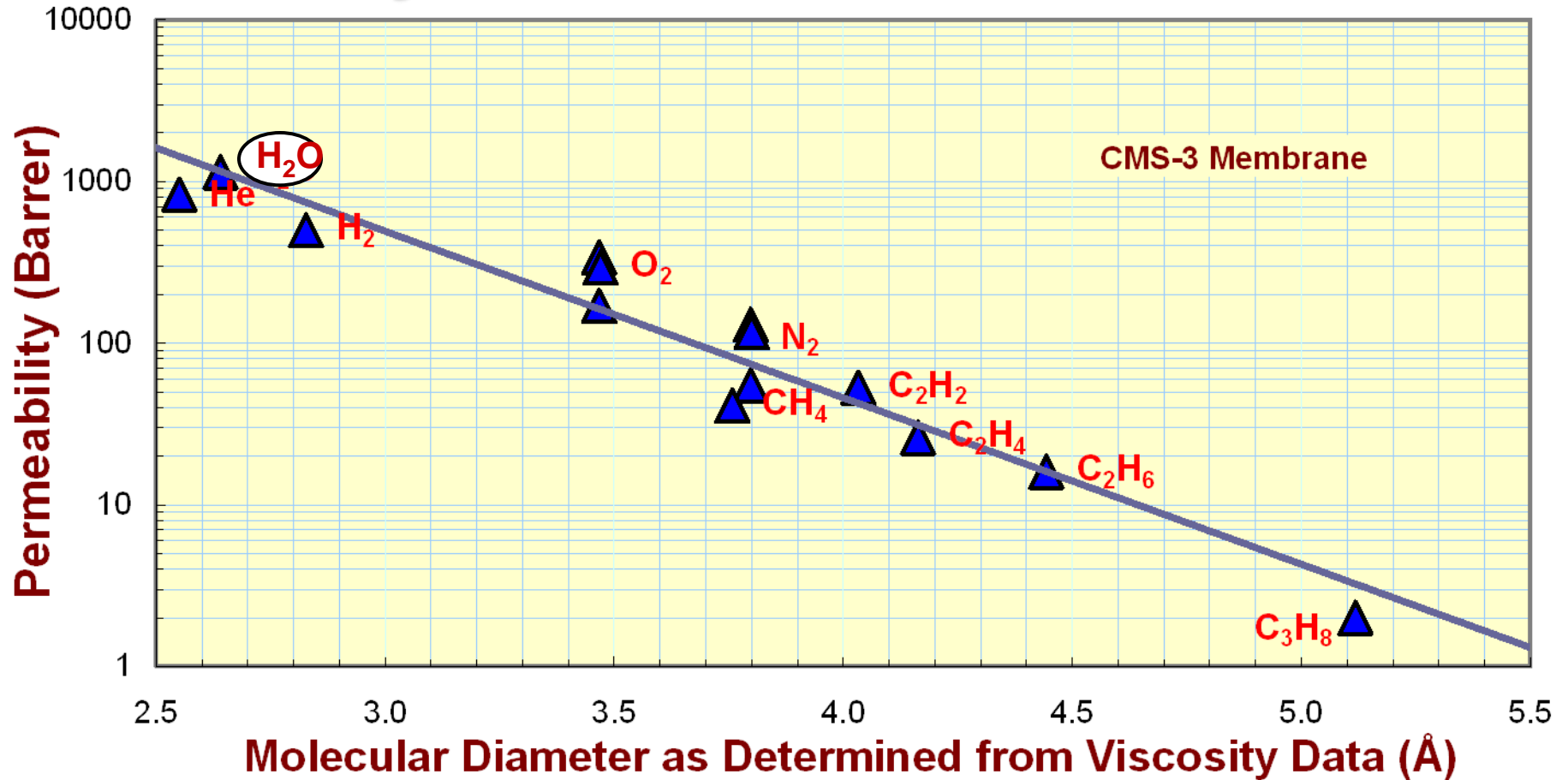
# THF Background (cont.)

- 2010 global demand 525 million Kg/yr
- 6.5% global growth rate
- Uses
  - PTMEG → Spandex fiber
  - Polyols
  - Copolyester
  - Pharma solvent

# CMS Membrane Characteristics

- **Glassy Membrane**
  - Transports atmospheric gasses
  - Retains hydrocarbons larger than  $C_2$
- **PTFE-like Polymers**
  - Excellent chemical and thermal resistance
  - Resistant to oxidation reactions
- **Extremely High Gas/Vapor Permeance**
  - Small membrane devices and associated equipment
- **Repels Hydrocarbons**
  - Non-fouling
  - Retains flux over time

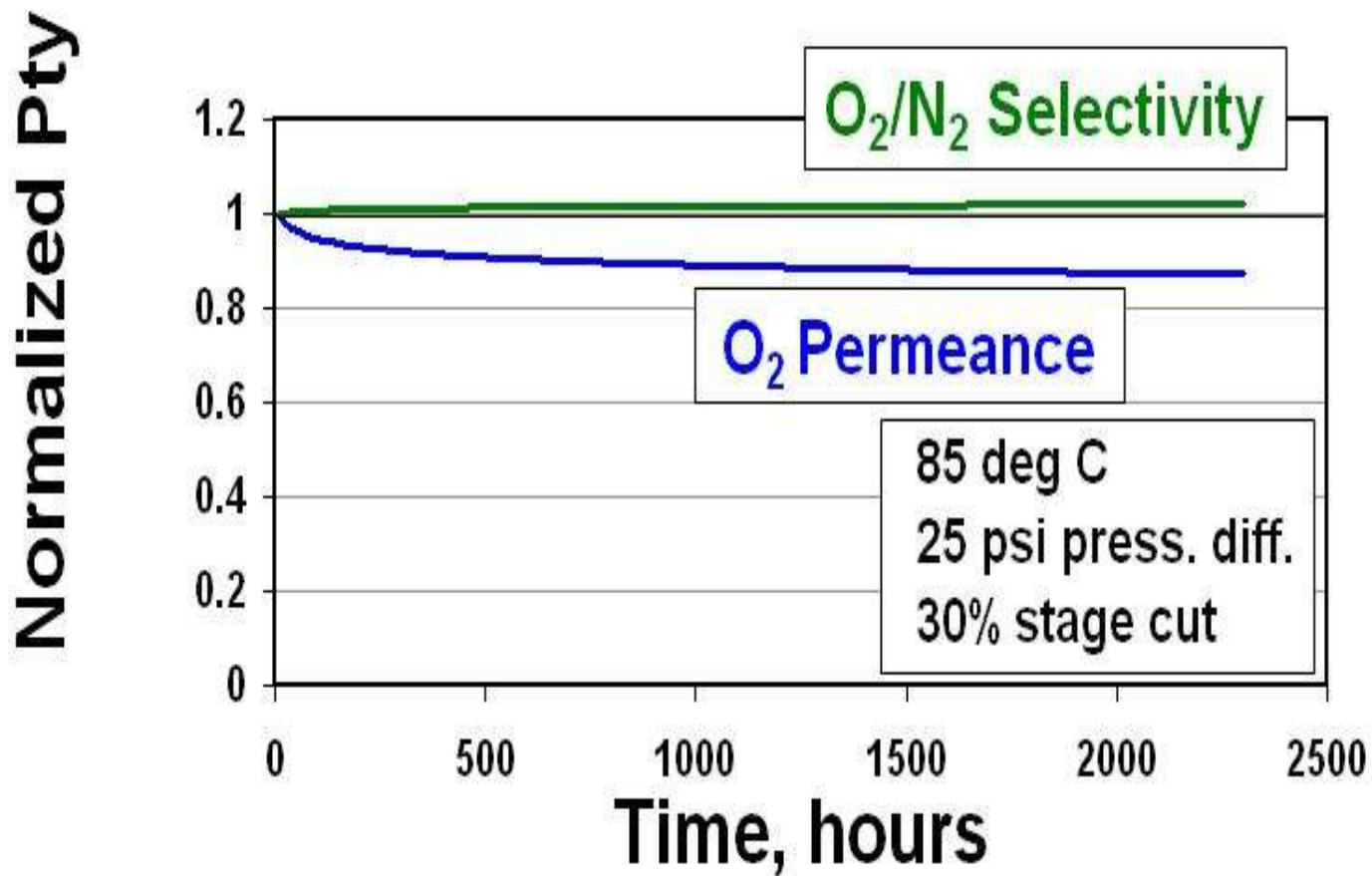
# Permeability vs. Molecular Diameter of Gases



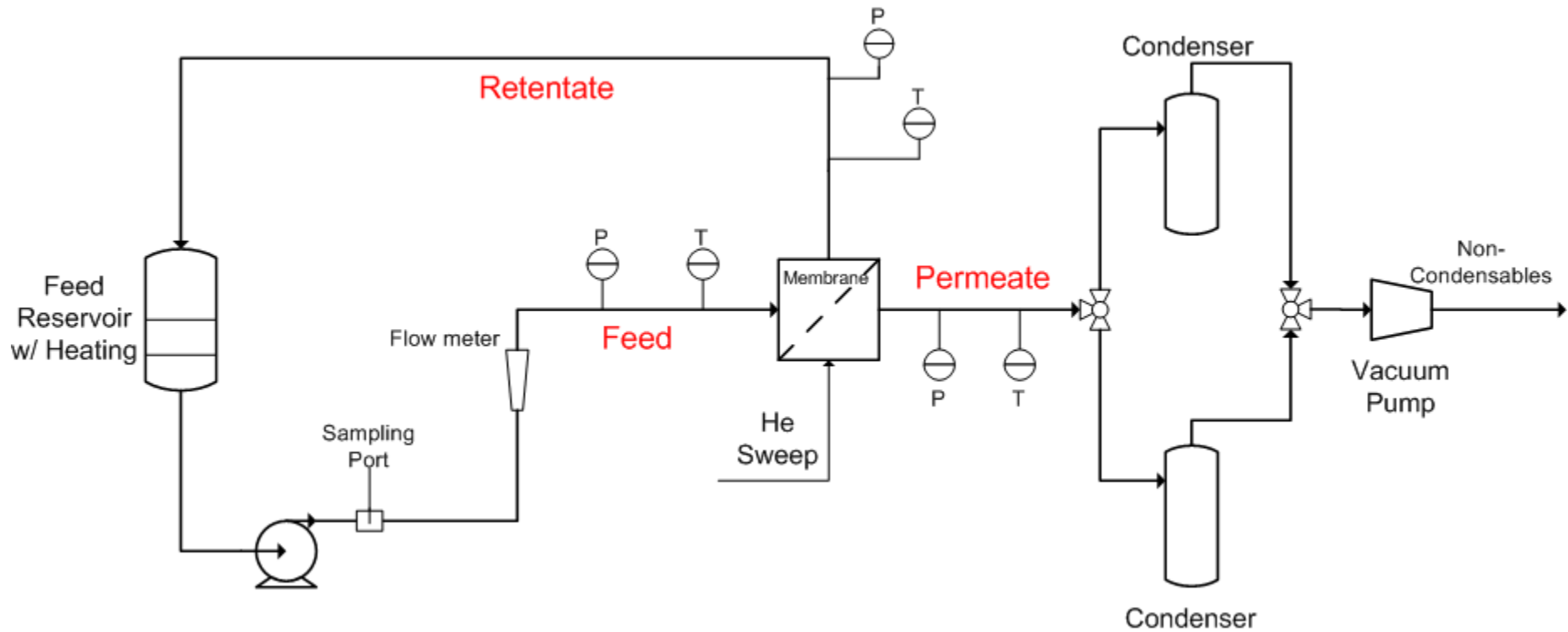
# CMS Membrane Chemical Resistance

<b>Reagent</b>	<b>Temperature °C</b>	<b><math>\Delta</math> Wt %</b>	<b>Appearance Change</b>
Carbon Tetrachloride	23	0	None
12 N HCl	60	0	None
Hexanes	23	0	None
MEK	23	0	None
44% NaOH	60	0	None
Perclene®	23	-0.1	None
Ethanol	23	0	None
Mineral Oil	60	0	None

# CMS Membrane Stability



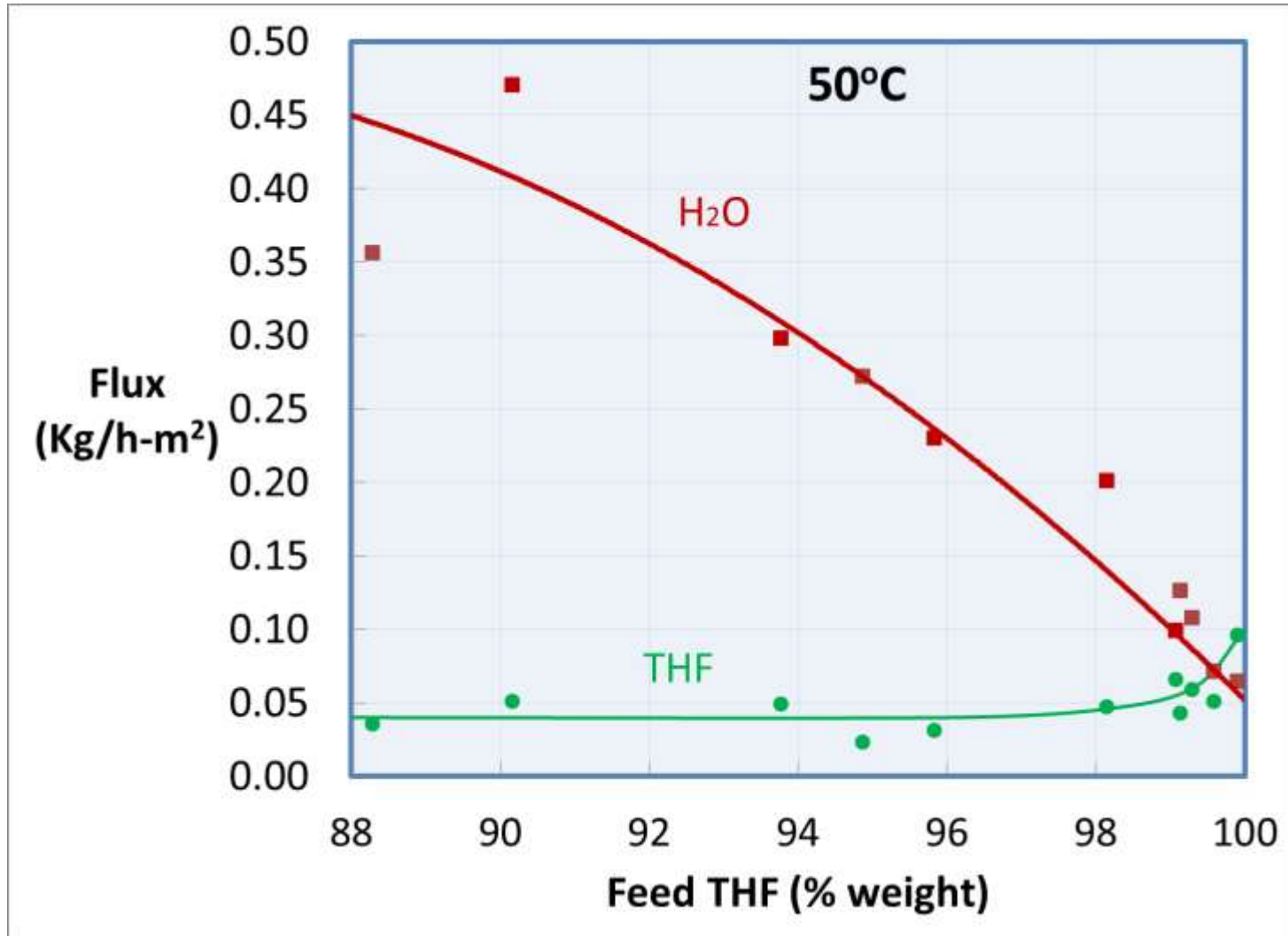
# Lab Pervaporation



# Test Conditions

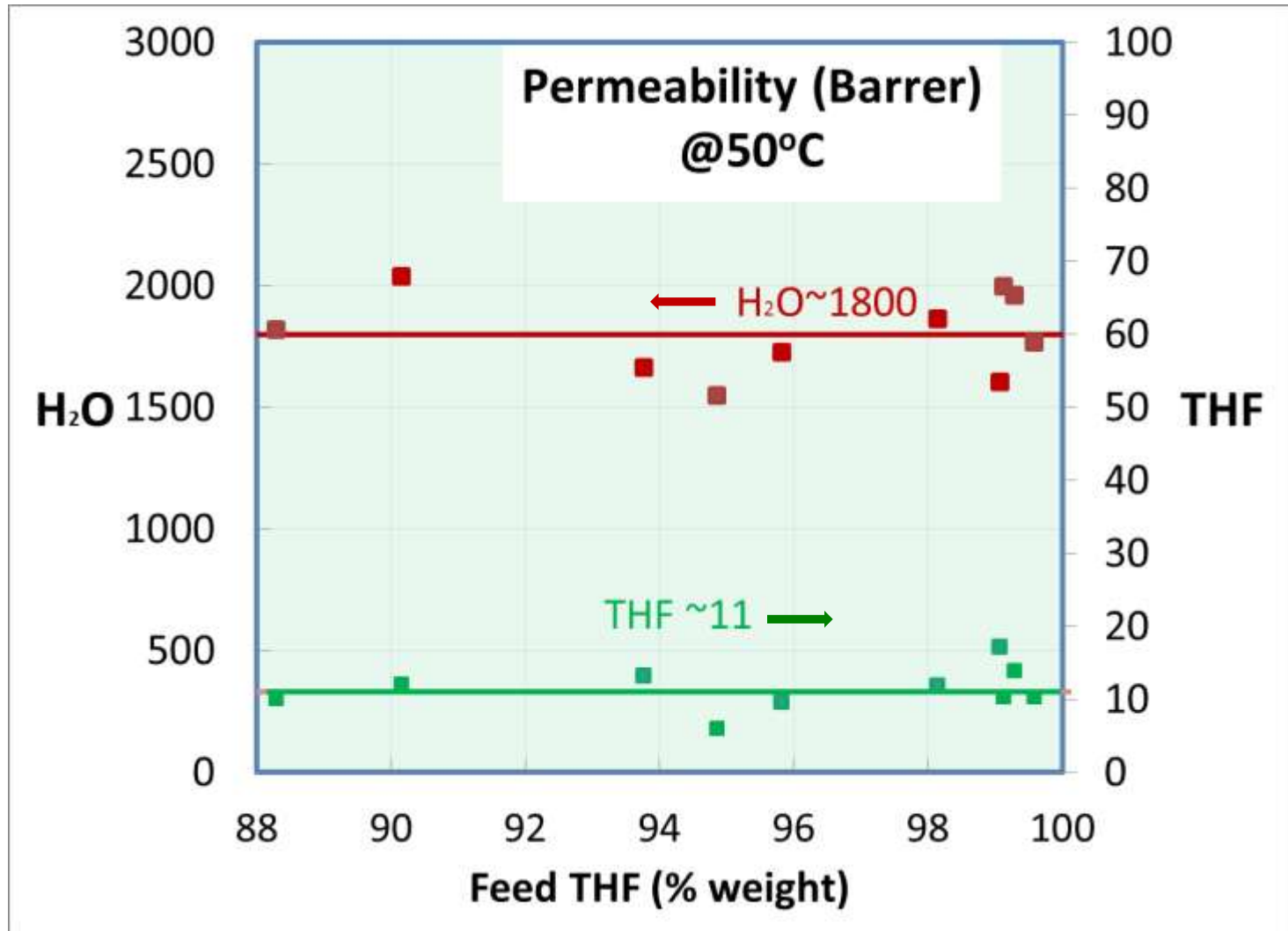
- Composite membrane, 14 cm<sup>2</sup>
- 1 micron
- Stirred cell to minimize boundary layer effect
- Permeate at 0.3 Psia (15 torr)
- Effect of THF feed concentration: 88-99+%
  - Next 3 charts
- Effect of temperature: 48-78°C
  - Following 3 charts

# Pervaporation of THF-Water flux vs. conc.

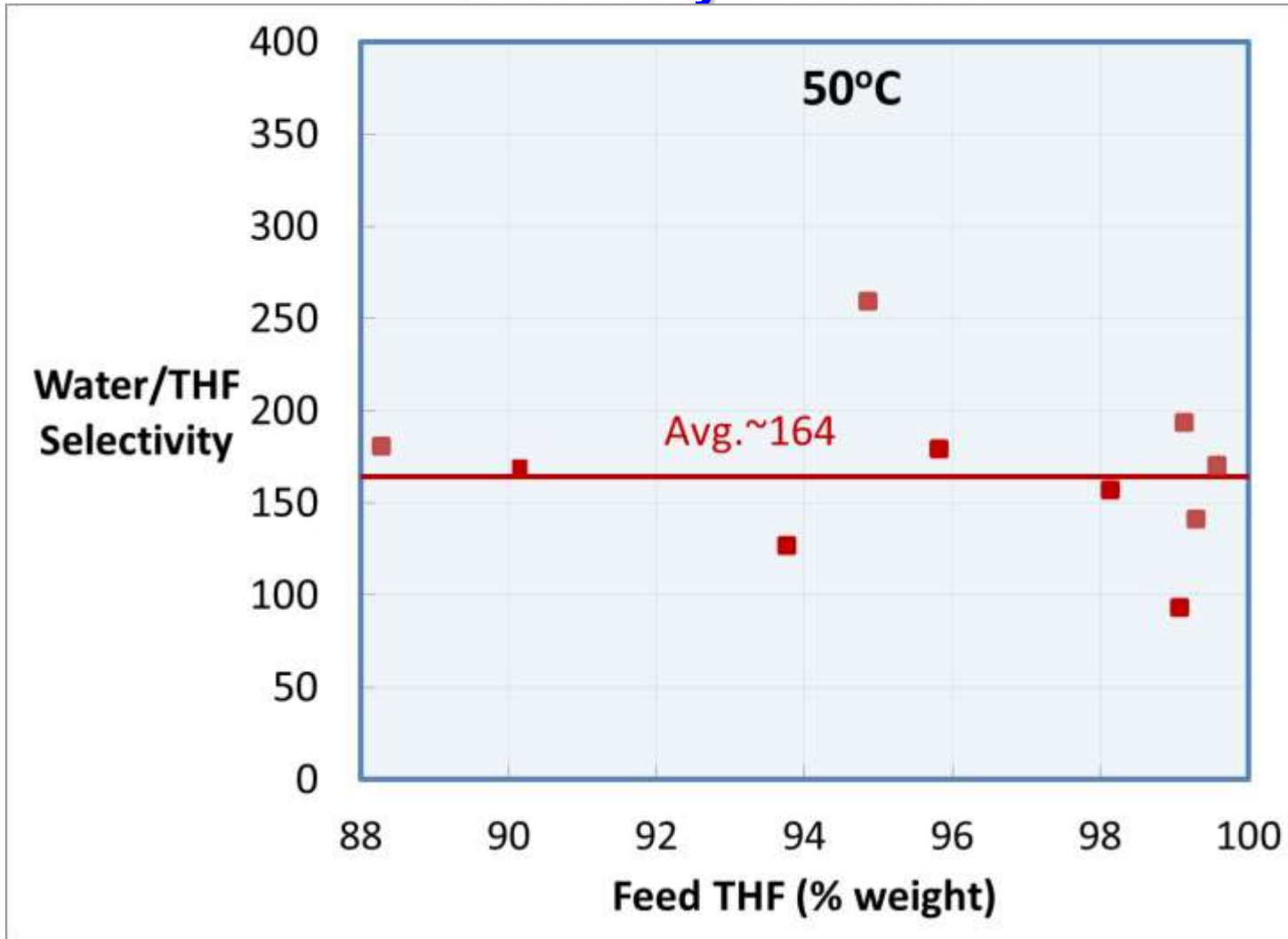


# Pervaporation of THF-Water

## Permeability vs. conc.

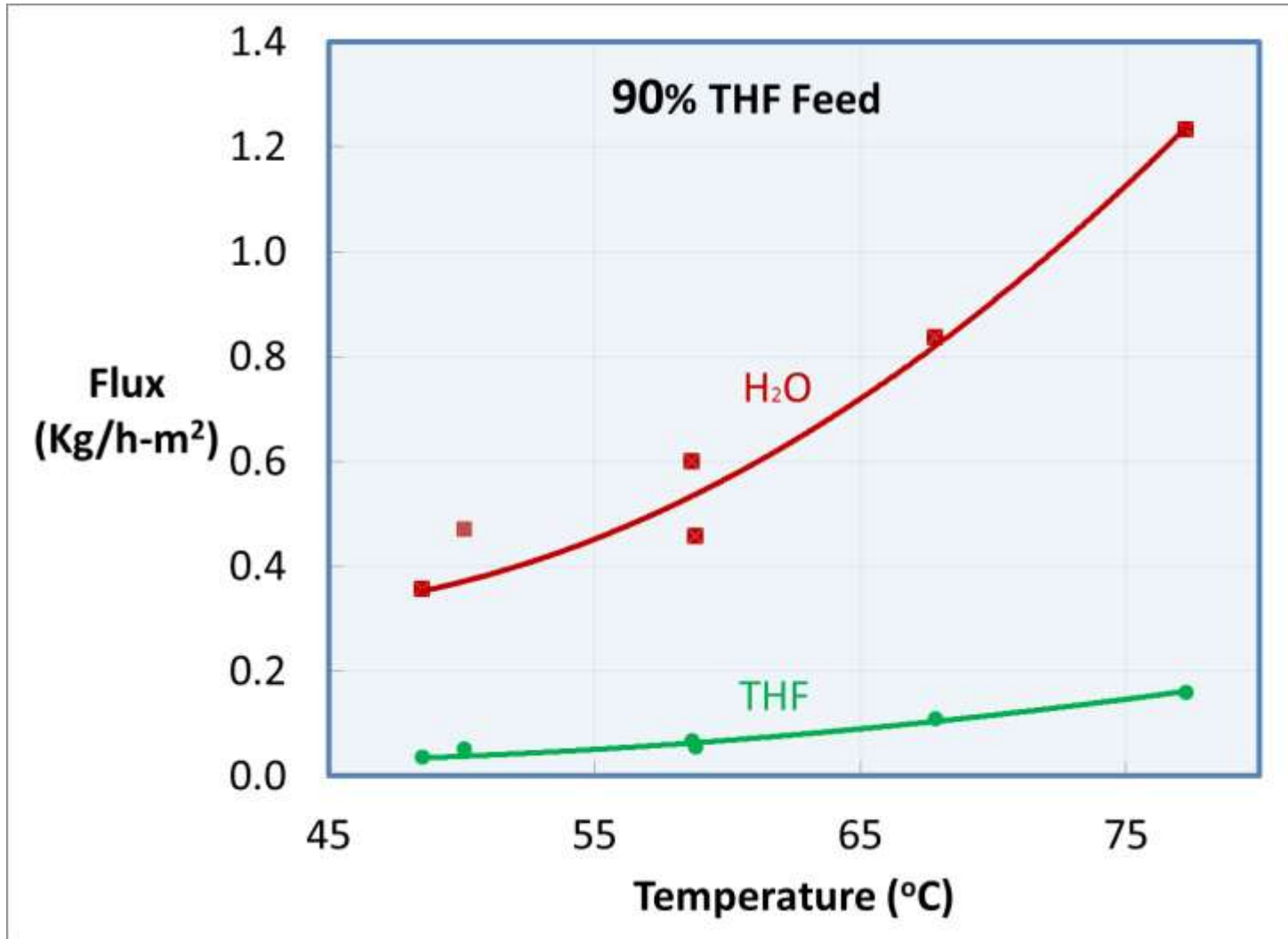


# Pervaporation of THF-Water Selectivity vs. conc.



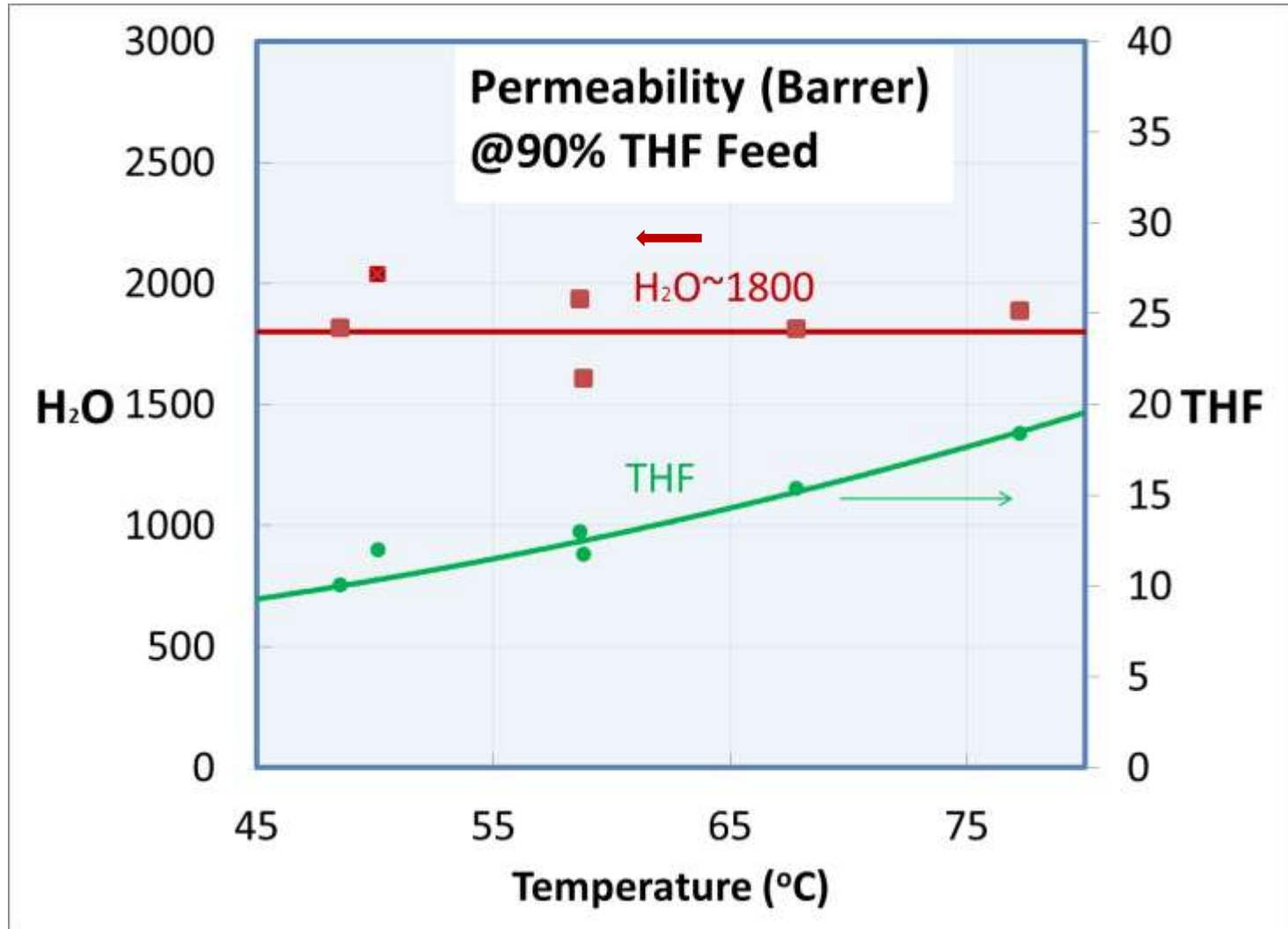
# Pervaporation of THF-Water

## Flux vs. Temp.

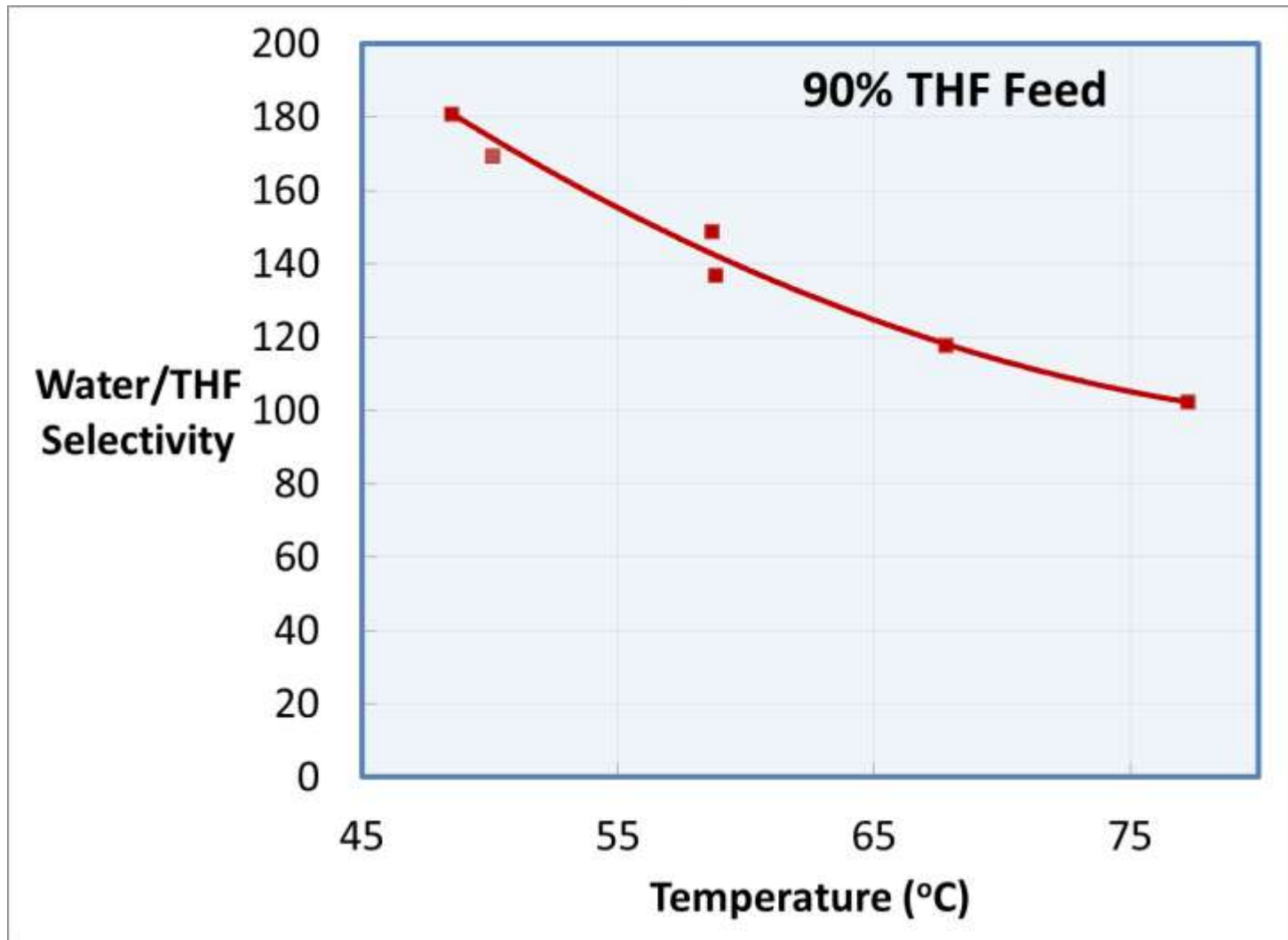


# Pervaporation of THF-Water

## Permeability vs. Temp.



# Pervaporation of THF-Water Selectivity vs. Temp.



# CMS vs. PVA

## Pervaporation of 95% THF @50°C

<b>Membrane</b>	<b>water flux (kg/m<sup>2</sup>-h)</b>	<b>Selectivity</b>
CMS3	0.26	164
Sulzer PVA*	0.14	273

\*Journal of Environmental Science and Health Part A (2008) 43, 1673–1684

# Fouling Resistance

Pervaporation test @50°C with “dirty” THF/water



CMS Perfluorinated membrane  
after 5-day test

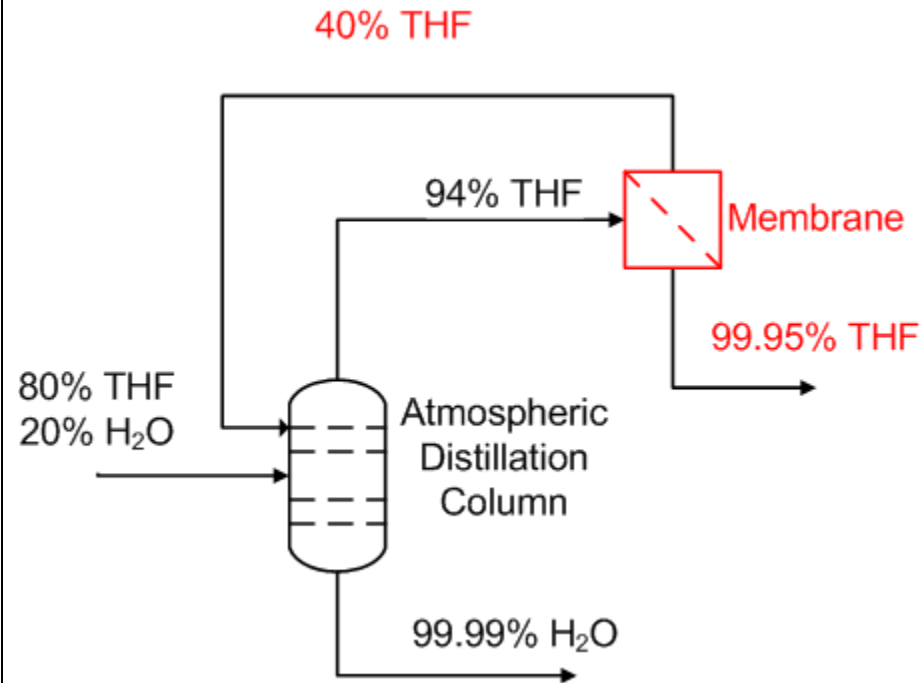
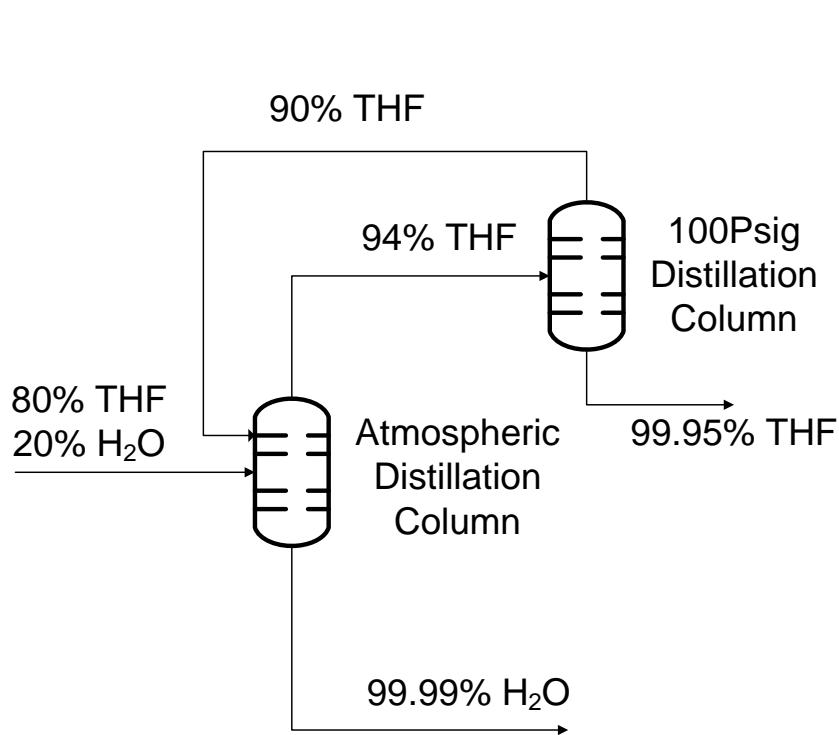


Hydrophilic membrane  
after 1-day test

# Module components resistant to THF @100°C

- month soaking test of membrane, porous support, potting materials show excellent stability

# Azeotropic distillation vs. Membrane



# Future Activities

- **Build large modules**
- **Testing in Pilot Scale Stream**
- **Field test**
- **Refinements in Process Modeling**
- **Economic analysis**
  - **Retrofit**
  - **Greenfield**

# Concluding Remarks

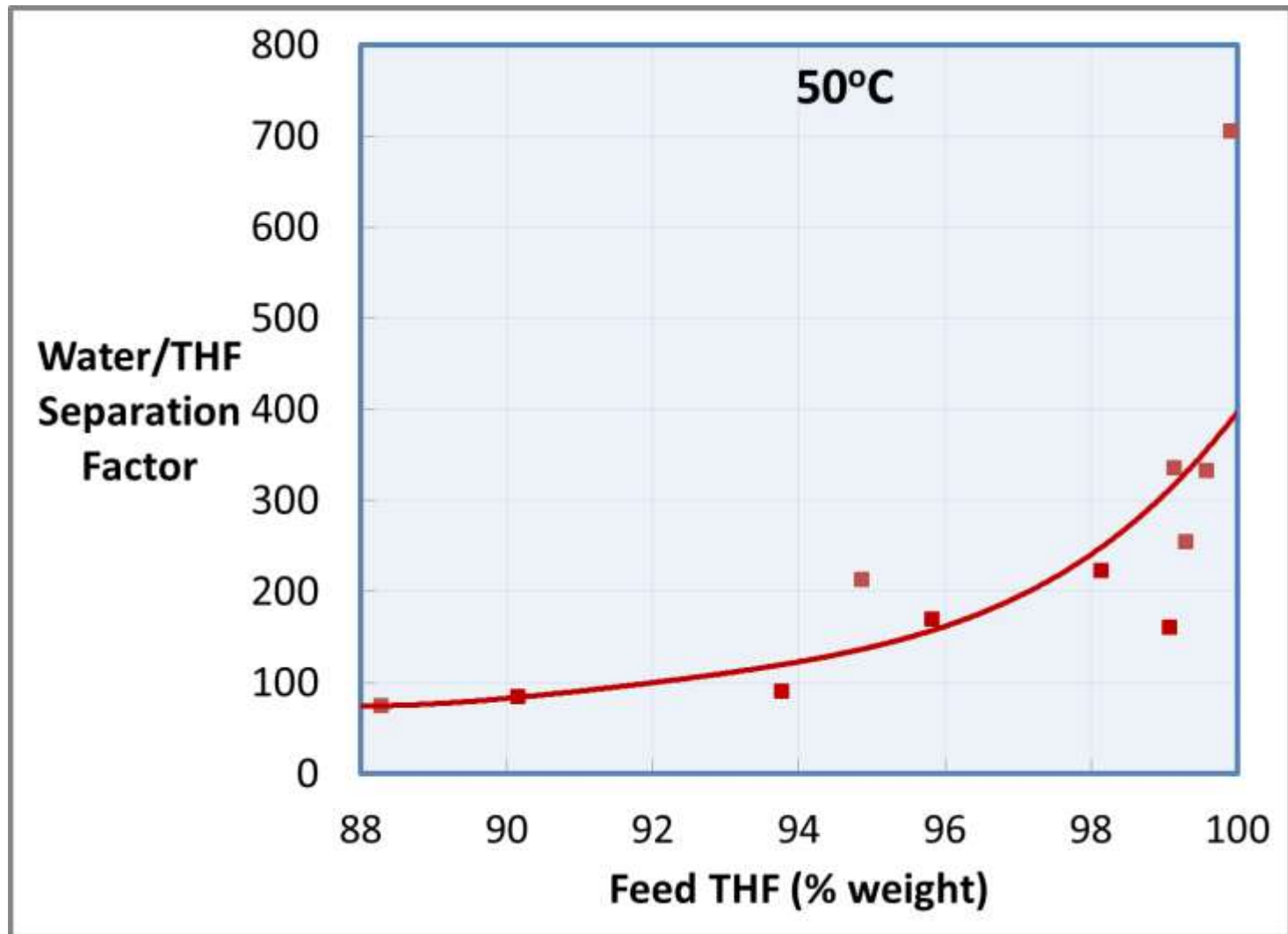
- **A hydrophobic perfluoropolymer membrane for efficient and selective removal of water from THF has been demonstrated.**
- **Membrane water permeability does not vary appreciably with THF concentration or temperature.**
- **Selectivity decreases moderately with temperature from 164 (48°C) to 100 (78°C)**
- **CMS has identified a process and associated membrane system that may offer cost advantages over conventional azeotropic distillation.**

# Acknowledgement

The authors gratefully acknowledge the SBIR grant support from the **Department of Energy**

# Pervaporation of THF-Water

## Sep. factor vs. conc.



# Pervaporation of THF-Water

## Sep. factor vs. Temp.

